

PATENT SPECIFICATION

(11) 1 413 315

1 413 315

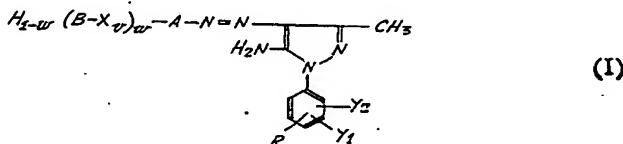
(21) Application No. 57141/72 (22) Filed 11 Dec. 1972
 (31) Convention Application No. 2 161 761 (32) Filed 13 Dec. 1971 in (19)
 (33) Germany (DT)
 (44) Complete Specification published 12 Nov. 1975
 (51) INT CL² C09B 62/74
 (52) Index at acceptance
 C4P 114 116 118 124 126 140 1A3A 1A3B 1B3 1D3 1F1
 1F3 1F6 1H4 2G2AY 2H18 2H1 2H21 2H5 2H9
 9A3A5 9A3B1 9A3F



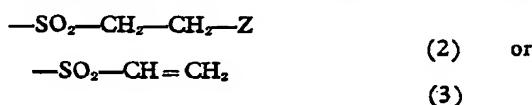
(54) WATER-SOLUBLE REACTIVE AZO DYESTUFFS

(71) We, HOECHST AKTIENGESELLSCHAFT, formerly known as Farbwelke Hoechst Aktiengesellschaft, vormals Meister Lucius & Brüning, a Body Corporate recognised under the Laws of the Federal Republic of Germany, of 6230 Frankfurt (M)-Hoechst, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides water-soluble reactive azo dyestuffs of the general formula



10 in which each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen or halogen atom or an alkyl, preferably having up to 4 carbon atoms, nitro, alkoxy, preferably having up to 4 carbon atoms, sulpho, carboxy, or a carbonyl acylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents an aryl or aromatic-heterocyclic radical; X represents $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{N}=\text{N}-$, $-\text{CH}_2-$, $-\text{NH}-$, $-\text{NH}-\text{CO}-\text{NH}-$, $-\text{NH}-\text{CO}-$ or $-\text{NH}-\text{SO}_2-$; R represents a group of the formula



20 in which Z represents a hydroxy group or a radical capable of being split off by an alkaline agent; and each of v and w , which may be identical or different, represents zero or one; and salts of compounds of the formula I, preferably alkali metal salts.

As radicals Z, capable of being split off by an alkaline agent, there may be mentioned for example: a halogen atom, preferably a chlorine or bromine atom; an alkylsulphonyloxy group, especially a methylsulphonyloxy group; an alkylsulphonylamino group, especially an N-methylsulphonyl-N-methylamino group; an arylsulphonyloxy group, especially a *p*-tolylsulphonyloxy or phenylsulphonyloxy group; an arylsulphonyl-amino group, especially an N-*p*-tolylsulphonyl-N-methylamino group; an aliphatic carbonyl acyloxy group, especially an acetoxy, propoxy, β -carboxy-propoxy or β -carboxy-acryloxy group; an aromatic carbonyl acyloxy group, especially a 3-sulphobenzoyloxy, benzoxyloxy or N-phenyl-carbamoyloxy ($\text{C}_6\text{H}_5\text{-NH-CO-O-}$) group; an aryl-oxy group, especially a phenoxy group, a di-alkyl-amino group, especially a dimethyl-amino or diethylamino group; a trialkylammonium group; and especially a thiosulphato group ($\text{HO}_3\text{S}-\text{S}-$) or a phosphato group ($\text{H}_2\text{O}_3\text{P}-\text{O}-$) and more especially a sulphato group ($\text{HO}_3\text{S}-\text{O}-$). The alkyl radicals are preferably lower alkyl radicals.

The radicals represented by A and B, are preferably mononuclear or binuclear aryl or aromatic-heterocyclic radicals and may contain one or more of the same or different

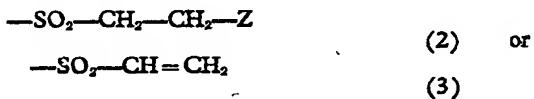
[Price 33p]

substituents selected from, for example, halogen atoms, e.g. fluorine, chlorine or bromine atoms, sulpho, sulphamoyl, N-alkyl-sulphamoyl, N,N-dialkyl-sulphamoyl, N-alkyl-N-phenyl-sulphamoyl, N-phenyl-sulphamoyl, N-aralkyl-sulphamoyl, N,N-dialkyl-sulphamoyl, N,N-diaralkyl-sulphamoyl, alkylthio, benzylamino, carboxy, carbamoyl, N-alkyl-carbamoyl, N,N-dialkyl-carbamoyl, N-aralkyl-carbamoyl (especially N-benzyl-carbamoyl), N-phenyl-carbamoyl, alkoxy carbonyl, aryloxycarbonyl, arylsulphonyl (especially phenylsulphonyl), alkylsulphonyl, amino, N-alkylamino, N-phenyl-N-alkyl-amino, N,N-dialkylamino, alkanoylamino or arylcarboxylamino, (especially benzamido), N-aralkylamino, nitro, cyclohexyl, cyano, hydroxy, alkoxy, phenoxy, trifluoromethyl and alkyl groups, any phenyl radical being unsubstituted or substituted by one or more chlorine atoms or alkyl, sulpho and/or carboxy groups. The alkyl radicals or moieties are preferably lower alkyl radicals or moieties.

Alkyl groups and alkyl moieties herein may be linear or branched and preferably contain up to 5 carbon atoms, especially methyl, ethyl, propyl and *t*-butyl groups. The term "lower" used to qualify an alkyl radical or alkyl moiety denotes that the radical or moiety has up to 4 carbon atoms.

Advantageously, in a dyestuff of the general formula I or a salt thereof, each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen or halogen atom or an alkyl having up to 4 carbon atoms, nitro, alkoxy having up to 4 carbon atoms, sulpho, carboxy, or carbonyl acylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents an aryl or heterocyclic radical that is either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from halogen atoms, sulpho, sulphamoyl, N,N-dialkyl-sulphamoyl, N-alkyl sulphamoyl, N-aralkyl sulphonyl, diaraalkyl sulphamoyl, carboxy, carbamoyl, N-alkyl carbamoyl, N,N-dialkyl-carbamoyl, N-aralkyl-carbamoyl, alkoxy carbonyl, aryloxycarbonyl, alkylsulphonyl, amino, N-alkylamino, N-aralkylamino, N-carboxylacylamino, nitro, cyano, hydroxy, alkoxy, trifluoromethyl and alkyl groups, any alkyl groups having up to 4 carbon atoms; and X, R, v and w are defined as in claim 1.

Preferred dyestuffs according to the present invention are those of the general formula (1) or their salts in which each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen, chlorine or bromine atom or lower alkyl, lower alkoxy, nitro, sulpho, carboxy, lower alkanoylamino, benzamido, nitrobenzamido, phenylsulphonylamino or *p*-tolylsulphonylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents a benzene, naphthalene or benzothiazole radical either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from chloro, bromo, sulpho, sulphamoyl, N-lower alkyl-sulphamoyl, N,N-di-lower alkyl-sulphamoyl, N-benzyl-sulphamoyl, carboxy, carbamoyl, N-lower alkyl-carbamoyl, N,N-di-lower-alkyl-carbamoyl, N-phenyl-carbamoyl, N-benzyl-carbamoyl, lower alkoxy-carbonyl, lower alkyl-sulphonyl, amino, lower alkyl-amino, acetamido, benzamido, nitrobenzamido, nitro, cyano, hydroxy, lower alkoxy, lower alkyl and trifluoromethyl groups. X represents $—O—$, $—S—$, $—CO—$, $—SO_2—$, $—N=N—$, $—CH_2—$, $—NH—$, $—NH—CO—NH—$, $—NH—CO—$ or $—NH—SO_2—$; R represents a group of the formula



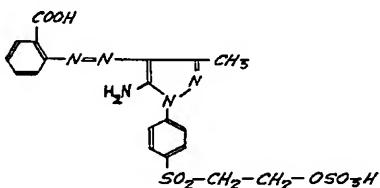
wherein Z represents a hydroxy, lower alkyl-sulphonyloxy, *p*-tolylsulphonyloxy, acetoxy, sulphobenzoyloxy, phenoxy, di-lower alkyl-amino, thiosulphato, phosphato, sulphato, N-lower alkyl-sulphonyl-N-methyl-amino or phenylsulphonyloxy group; and each of v and w , which may be identical or different, represents zero or one.

Particularly preferred dyestuffs according to the invention are those of the general formula (I) and their salts in which each of A and B, which may be identical or different, represents a benzene, naphthalene or benzothiazole radical either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from chloro, sulpho, carboxy, lower alkyl, lower alkoxy, lower alkanoylamino, benzamido, nitrobenzamido, nitro, cyano and N-phenyl-carbamoyl groups; and Y_1 , Y_2 , R, X, v and w are defined as in the preceding paragraph.

The azo dyestuffs of the invention are very well suited for the dyeing and printing of various fibrous materials containing nitrogen, for example wool, silk, synthetic polyamide, polyurethane, and leather, and particularly cellulose-containing fibrous materials,

for example cotton, regenerated cellulose and linen. The dyestuffs are preferably applied according to dyeing and printing methods generally used in industry and known for reactive dyestuffs. They yield dyeings and prints of high colour intensity. Especially on cellulosic fibres and in the presence of alkaline agents, for example sodium hydroxide, sodium bicarbonate, sodium carbonate or potassium carbonate, the dyeings and prints obtained are bright and have a very good fastness to light and wet processing as well as good fastness properties to washing. Application and fixation methods which may be used for dyeing and printing with the dyestuffs of the invention are described in, for example, *Mellands Textilberichte* 39, 66-67 (1958); *Journal of the Society of Dyers and Colourists* 75, 581-584 (1959); *Mellands Textilberichte* 46, 286-289 (1965); and *Textil-Praxis* 1968, 754-758. Moreover, the dyestuffs have an excellent absorptive power and a very good solubility.

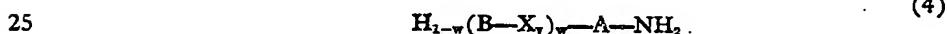
The azo dyestuffs of the present invention are also distinguished by an improved solubility, a substantially increased resistance to alkaline padding liquors or printing pastes, a substantially diminished sensitivity to metals and a far better tintorial strength when dyed or printed on wool or cellulosic fibrous materials, especially as compared with the azo dyestuff of the formula



described in German Patent Specification No. 925 121.

Additionally, the dyestuffs of the present invention, when applied according to printing methods, do not form spots since the unfixed portion can easily be removed by washing and thus a clear and sharp-outlined white bottom can be obtained.

The dyestuffs of the invention may be prepared by diazotizing an aromatic amine of the general formula



and reacting the resulting diazonium compound with an amino-pyrazole of the general formula



in which formulae the symbols are defined as above, in a weakly acid or neutral medium or in a medium rendered alkaline by sodium bicarbonate or sodium carbonate.

The dyestuff may be isolated by salting out, for example with sodium or potassium chloride, by spray-drying the reaction mixture or by acidifying the solution, whereupon the dyestuff precipitates as an inner salt.

In a resulting dyestuff the group represented by R may be converted to another group represented by R.

A resulting dyestuff of the general formula (1) in which R represents a β -hydroxyethylsulphonyl group may be converted into a dyestuff of the formula (1) in which R represents a β -sulphato-ethylsulphonyl group in known manner by means of a sulphating agent, for example concentrated sulphuric acid, chlorosulphonic acid, amidosulphonic acid or an agent yielding sulphur trioxide.

A dyestuff of the general formula (1) in which R represents a β -hydroxyethylsulphonyl group may be converted into one in which R represents a β -phosphatoethylsulphonyl group in known manner with a phosphating agent, for example concentrated phosphoric acid, pyrophosphoric acid, metaphosphoric acid, polyphosphoric acid, a polyphosphoric acid alkyl ester, phosphoroxy chloride or a mixture of phosphoric acid and phosphorus pentoxide.

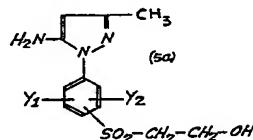
Such known methods have been described, for example, in Houben Weyl, *Methoden der organischen Chemie*, vol. 12/2, pages 147 et seq.

5 A dyestuff of the general formula (1) in which Z represents an alkylsulphonyloxy, arylsulphonyloxy or acyloxy group may be obtained from one in which Z represents a hydroxy group by reacting the latter in known manner with an (alkyl or aryl)-sulphonic acid chloride, for example methanesulphonyl chloride or *p*-toluenesulphonyl chloride, or with a carboxylic acid chloride, for example acetyl chloride or 3-sulphobenzoyl chloride.

10 A dyestuff in which R represents a vinylsulphonyl group may be obtained in known manner from one in which R represents a group of the formula (2) by treatment with an alkaline agent, for example sodium carbonate or sodium hydroxide.

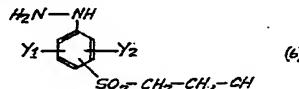
15 A dyestuff in which Z represents a thiosulphato group or a dialkylamino group may be prepared in known manner from a dyestuff in which R represents a vinylsulphonyl group by reaction with a thiosulphate, for example sodium thiosulphate, or with a dialkylamine, for example diethylamine, respectively.

15 An amino-pyrazole of the general formula (5) in which R represents a vinylsulphonyl group or a group of the formula (2) in which Z represents a radical capable of being split off by an alkaline agent, may be obtained, for example, from an amino-pyrazole of the general formula

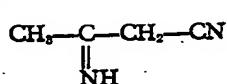


20 by known method, for example by the methods disclosed above for the inter-conversion of dyestuffs of the general formula (1).

20 An amino-pyrazole of the general formula (5a), which may be used for the preparation of the dyestuffs of the general formula (1) may be prepared in the usual manner by reacting a phenyl hydrazine derivative of the formula



25 with diacetonitrile of the formula

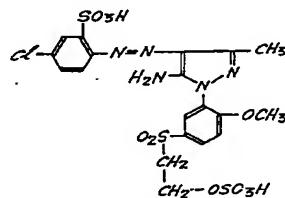


The following Examples illustrate the invention. The parts and percentages are by weight unless stated otherwise and the relationship of parts by weight to parts by volume is that of a gram to a cubic centimetre.

30 EXAMPLE 1.
30 20.8 Parts of 2-sulpho-4-chloroaniline were diazotized in a conventional manner. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulfonyl)-35 phenyl-3-methyl-pyrazole amine-(5) were added, and the mixture was stirred at a pH-value of from 6 to 7 until coupling was complete. After addition of potassium chloride, the dyestuff was suction-filtered and dried at 60°C in vacuo.

35 66 Parts of a yellow powder were obtained, which dissolved in water to give a yellow solution.

The dyestuff obtained corresponds, in the form of the free acid, to the formula



40 and dyes wool and cellulose fiber materials brilliant greenish yellow shades. The dyeings and prints have very good fastness properties to light and wet processing. Moreover, the cotton prints show a clear white bottom.

EXAMPLE 2.

20.8 Parts of 4-chloroaniline-2-sulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 31.1 parts of 1-(2'-methoxy-5'- β -hydroxyethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred in a medium rendered alkaline by means of sodium carbonate, until coupling was complete. The solution was neutralized and the dyestuff was precipitated as the salt by the addition of potassium chloride, it was suction-filtered and dried at 60°C in vacuo.

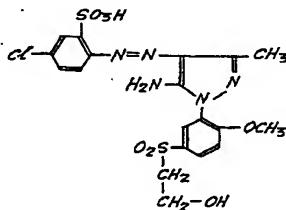
For converting it into sulphuric acid monoester the dyestuff was finely ground, introduced into 400 parts of concentrated sulphuric acid and stirred until completely dissolved. The reaction mixture was then poured onto 900 parts of ice. The dyestuff was suction-filtered, washed to neutral with a 25% potassium chloride solution and dried at 60°C in vacuo. It was identical with the dyestuff obtained according to Example 1.

15 60 Parts of the dyestuff of the formula

5

10

15



20 as prepared according to Example 2, paragraph 1, were introduced at 85—90°C into 250 parts of pyridine. Subsequently, 7.4 parts of urea and 42 parts of amidosulfonic acid were added and the mixture was heated for half an hour to 100—105°C. The mixture was then poured onto 2500 parts of water and the dyestuff was isolated by salting it out with potassium chloride. The dyestuff was suction-filtered and washed with a 25% potassium chloride solution.

20

25 The products obtained is identical with the dyestuff obtained according to Examples 1 and 2.

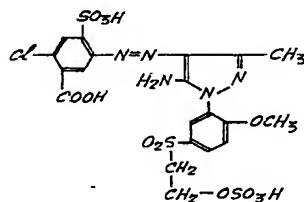
25

25.2 Parts of 4-chloro-5-carboxy-aniline-2-sulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred in a weakly acid medium until coupling was complete. The reaction solution was acidified by means of a mineral acid and the dyestuff was suction-filtered and dried at 60°C in vacuo.

30

30 The dyestuff corresponds, in the form of the free acid, to the formula

30



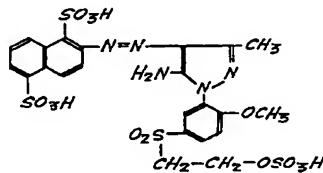
35 yields on wool and cellulose fiber material, in the presence of acid-binding agents, bright greenish yellow dyeings and prints having excellent fastness properties to light and washing. Moreover, the prints have a clear white bottom.

35

30.3 Parts of 2-naphthylamine-1,5-disulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred in a medium which had been rendered alkaline by means of sodium bicarbonate, until coupling was complete. The dyestuff was isolated by salting out with potassium chloride, suction-filtered and dried at 60°C in vacuo.

40

In the form of the free acid, the dyestuff corresponds to the formula



On wool and cellulose fibers, it yields bright greenish yellow dyeings and prints having good fastness properties to light and wet processing and a clear white bottom.

5

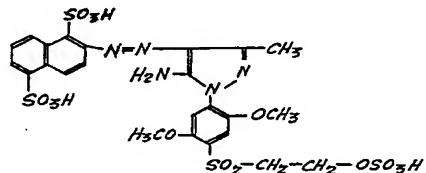
30.3 Parts of 2-naphthylamine-1,5-disulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 42.1 parts of 1-(2',5'-dimethoxy-4'-sulfatoethylsulfonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred in a medium which had been rendered alkaline by means of sodium bicarbonate, until coupling was complete. The dyestuff was isolated by adding potassium chloride, suction-filtered and dried at 60°C in vacuo.

10

5

10

In the form of the free acid, the dyestuff corresponds to the formula



15

On wool and cellulose fibers, the dyestuff yields according to known methods bright yellow dyeings and prints having good fastness properties to light and wet processing.

15

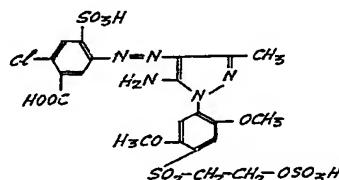
EXAMPLE 7.

20

25.2 Parts of 4-chloro-5-carboxy-aniline-2-sulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 42.1 parts of 1-(2'-5''-dimethoxy-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred under neutral conditions until coupling was complete. The dyestuff solution was acidified by means of a mineral acid, the dyestuff was salted out by means of potassium chloride, suction-filtered and dried at 60°C in vacuo.

20

In the form of the free acid, the dyestuff obtained corresponds to the formula



25

On wool and cellulose fiber materials, the dyestuff yields yellow dyeings and prints having very good fastness properties to light and wet processing.

25

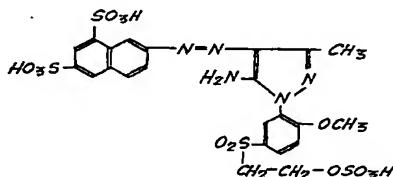
EXAMPLE 8.

30

30.3 Parts of 2-naphthylamine-6,8-disulphonic acid were diazotized in a conventional manner. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added, the mixture was neutralized by means of sodium bicarbonate and stirred until coupling was complete. By adding potassium chloride, the dyestuff was salted out, suction-filtered and dried at 60°C.

30

In the form of the free acid, the dyestuff corresponds to the formula



It dyes wool and cellulose fiber materials yellow shades fast to wet processing. The prints obtained according to cotton printing processes as usual for reactive dyestuffs have a clear white bottom.

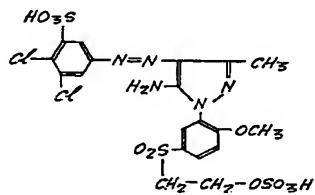
5

EXAMPLE 9.

24.2 Parts of 3,4-di-chloroaniline-5-sulphonic acid were diazotized by a conventional method. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'-β-sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added, the mixture was neutralized by adding sodium bicarbonate and stirred until coupling was complete. The dyestuff was isolated after sodium chloride had been added and it was dried at 60°C in vacuo.

10

In the form of the free acid, the product obtained corresponds to the formula



According to the usual methods, bright greenish yellow dyeings and prints having very good fastness properties to light and wet processing, are obtained on wool and cotton. The prints moreover show a clear white bottom and very sharp outlines.

15

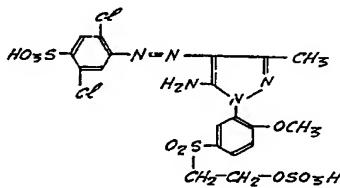
EXAMPLE 10.

24.2 Parts of 2,5-dichloroaniline-4-sulphonic acid were diazotized by a conventional method. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'-β-sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added, the mixture was neutralized by means of sodium bicarbonate and stirred until coupling was complete. The dyestuff was salted out after potassium chloride had been added and it was dried at 60°C in vacuo.

20

In the form of the free acid, the product obtained corresponds to the formula

25



Bright greenish yellow dyeings and prints having excellent fastness to light and very good fastness to wet processing are obtained on wool and cellulose fiber materials. In addition, the prints show a clear white bottom.

30

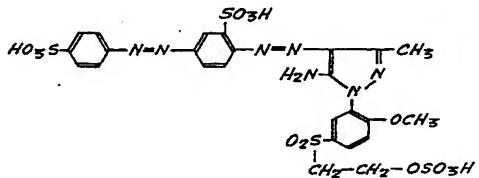
EXAMPLE 11.

34.7 Parts of 4-amino-azobenzene-3',4-disulfonic acid were diazotized by a conventional method. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'-β-sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added, the pH of the mixture was adjusted to 6 by means of sodium hydrogencarbonate and the solution

30

was stirred until coupling was complete. The dyestuff was salted out by means of potassium chloride, suction-filtered and dried at 60°C in vacuo.

In the form of the free acid, the dyestuff corresponds to the formula



5 and yields, according to usual methods, on wool and cellulose fiber materials, very intense, yellowish red dyeings and prints having excellent fastness to light and good fastness to wet processing.

5

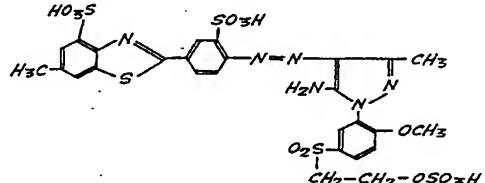
EXAMPLE 12.
10 40 Parts of dehydro-4-thioluidine-disulfonic acid were diazotized by a conventional method and 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added. The mixture was neutralized by means of sodium bicarbonate and stirred until coupling was complete. After addition of sodium chloride, the dyestuff was salted out, suction-filtered and dried at 60°C in vacuo.

10

In the form of the free acid the product obtained corresponds to the formula

15

15



According to the usual methods, the dyestuff yields, on wool and cellulose fiber materials bright yellow dyeings and prints fast to light and washing and showing a very good color build-up.

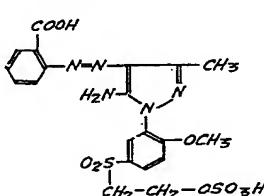
EXAMPLE 13.

20 13.7 Parts of 1-aminobenzene-2-carboxylic acid were diazotized by a conventional method. To the diazonium salt solution, 39.1 parts of 1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added. The mixture was neutralized by means of sodium bi-carbonate and stirred until coupling was complete. By adding potassium chloride, the dyestuff was salted out, suction-filtered and dried at 60°C in vacuo.

20

25 In the form of the free acid, the product obtained corresponds to the formula

25



30 According to the usual methods, bright greenish yellow dyeings and prints having very good fastness properties to light and washing were obtained on wool and cellulose fibers. The prints also show a clear white bottom and sharp outlines.

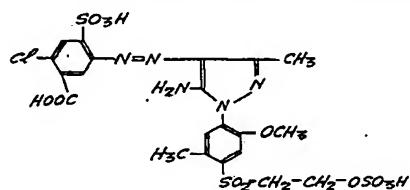
30

EXAMPLE 14.

35 25.2 Parts of 4-chloro-5-carboxy-aniline-2-sulfonic acid were diazotized by a conventional method. To this diazonium salt solution, 40.5 parts of 1-(2'-methoxy-5'-methyl-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were added and the mixture was stirred at a pH value of 6—7, until coupling was complete. At a pH of 4, the dyestuff was salted out by means of potassium chloride, suction-filtered and dried at 60°C in vacuo.

35

In the form of the free acid, the product obtained corresponds to the formula

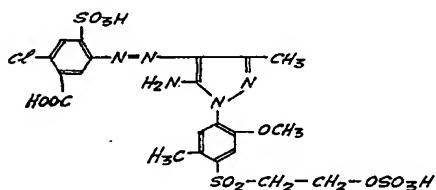


and, according to known methods, it yields on wool and cellulose fiber materials, yellow dyeings and prints fast to light and washing. The prints moreover show sharp outlines.

5

EXAMPLE 15.

50 Parts of an aqueous 38% diethylamine solution were added to 63.7 parts of the dyestuff of the formula



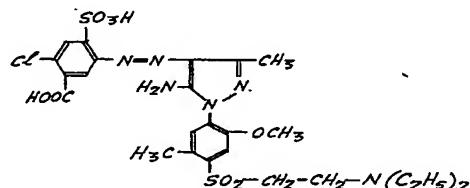
10

(prepared according to Example 14). In the course of 30 minutes, 5 parts of a 33% sodium hydroxide solution were added dropwise. Stirring was then continued for 1 hour at 60—70°C and at a pH-value of 1 to 12.

10

After cooling, the pH was adjusted to 5 by means of a dilute mineral acid and the dyestuff was salted out by means of potassium chloride. In the form of the free acid, the dyestuff corresponds to the formula

15

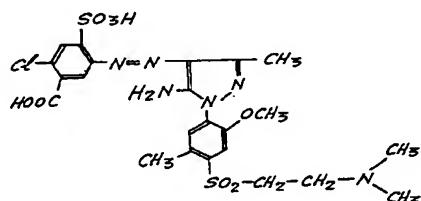


20

Printing pastes containing alkaline agents and this dyestuff were stable for a prolonged period of time. Such printing pastes yield on cellulose fiber materials greenish yellow prints having good fastness properties to light and wet processing. The color intensity of such prints did not change even after the printing paste had been kept for 14 days at room temperature.

20

Using, instead of the diethylamine solution, the equimolar amount of a dimethylamine solution, the dyestuff of the formula



was obtained, which has practically the same properties as the diethylamino derivative.

25

EXAMPLE 16.

25.2 Parts of 4-chloro-5-carboxyaniline-2-sulphonic acid were reacted according to Example 10 with 39.1 parts of 1-(2'-methoxy-5'-β-sulphatoethylsulphonyl)-phenyl-3-

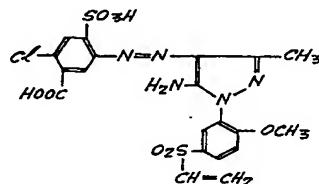
25

5

methyl-pyrazole-amine-(5). The pH-value of the dyestuff solution obtained was adjusted to 10—11 by means of a concentrated sodium hydroxide solution and the mixture was stirred for 1 hour in the cold. Subsequently, the pH was readjusted to 4 by means of concentrated hydrochloric acid. By adding sodium chloride the dyestuff was salted out, suction-filtered and dried at 60°C.

5

In the form of the free acid, the product obtained corresponds to the formula



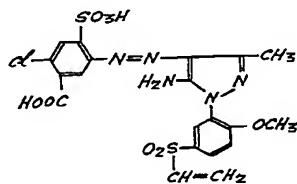
10

In the presence of alkaline agents, the dyestuff yields on cellulose fiber materials, greenish yellow dyeings and prints having excellent fastness properties to light and wet processing. The prints additionally show a clear white bottom.

10

EXAMPLE 17.

54.4 Parts of the dyestuff of the formula



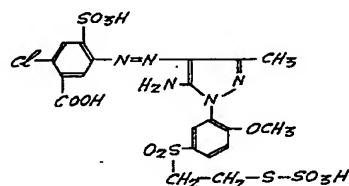
15

(prepared according to Example 16) were dissolved in 1500 parts of water at 60°C, 37.2 parts of crystallized sodium thiosulphate were added at a pH-value of 5 to 6 and the mixture was stirred for 6 hours at 60—65°C. The pH-value was maintained constant by adding dropwise dilute acetic acid. The dyestuff solution was filtered while hot and spray-dried.

15

In the form of the free acid, the dyestuff obtained corresponds to the formula

20



20

According to known methods, it yields on wool and cellulose fiber materials dyeings and prints of greenish yellow shade which are fast to light and washing. The prints moreover show sharp outlines and a clear white bottom.

25

31.1 Parts of 1-(2'-methoxy-5'-β-hydroxyethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5) were introduced at 130°C into 120 parts of polyphosphoric acid having a P2O5-content of 80%.

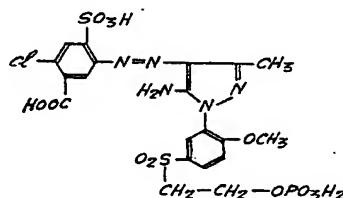
25

30

After 1 hour, the mixture was poured into 170 parts of water and stirred for 1 hour at 80—90°C. The inner salt which had precipitated was suction-filtered and added to a diazonium salt solution which had been prepared in a conventional manner from 25.2 parts of 4-chloro-5-carboxy-aniline-2-sulfonic acid. By adding sodium bicarbonate the solution was neutralized and stirred until coupling was complete. The dyestuff was salted out by means of potassium chloride, suction-filtered and dried at 60°C.

30

In the form of the free acid, the dyestuff corresponds to the formula



According to known methods, bright greenish yellow dyeings and prints having excellent fastness properties to light and wet processing are obtained on wool and cellulose fibre materials. The prints moreover show a clear white bottom and sharp outlines.

The dyestuffs indicated in the following Table show similar good fastness properties to light and wet processing.

Example	diazo component	coupling component	shade
19	2-naphthylamine-5,7-disulphonic acid	1-(2'-methoxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	yellow
20	2-naphthylamine-1,7-disulphonic acid	„	greenish-yellow
21	2-naphthylamine-5-sulphonic acid	„	yellow
22	2-naphthylamine-6-sulphonic acid	„	yellow
23	2-naphthylamine-3,6,8-trisulphonic acid	„	yellow
24	2-naphthylamine-4,6,8-trisulphonic acid	„	yellow
25	1-amino-naphthalene-3,6,8-trisulphonic acid	„	yellow
26	4-methyl-aniline-6-sulphonic acid	„	greenish-yellow
27	1-aminobenzene-2,5-disulphonic acid	„	greenish-yellow
28	1-aminobenzene-2,4-disulphonic acid	„	yellow
29	1-amino-2-methoxy-5-methyl-benzene-4-sulphonic acid	„	yellow
30	2-amino-4-chloro-benzene-carboxylic acid	„	greenish-
31	4-chloroaniline-2-sulphonic acid	1-(2'-methoxy-5'-methyl-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	greenish-yellow
32	2,5-dichloroaniline-4-sulphonic acid	„	greenish-yellow
33	3,4-dichloroaniline-5-sulphonic acid	„	greenish-yellow
34	1-aminobenzene-2-carboxylic acid	„	greenish-yellow
35	4-methyl-aniline-2-sulphonic acid	„	greenish-yellow
36	2-naphthylamine-1,5-disulphonic acid	„	yellow

Example	diazo component	coupling component	shade
37	2-naphthylamine-1,7-disulphonic acid	1-(2'-methoxy-5'-methyl-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	yellow
38	2-naphthylamine-6,8-disulphonic acid	„	yellow
39	2-naphthylamine-5,7-disulphonic acid	„	yellow
40	1-aminobenzene-2-sulphonic acid	„	greenish-yellow
41	1-aminobenzene-4-sulphonic acid	„	greenish-yellow
42	1-aminobenzene-2,5-disulphonic acid	„	yellow
43	4-aminoazobenzene-3,4'-di-sulphonic acid	„	yellowish-red
44	4-chloroaniline-6-sulphonic acid	1-(2',5'-dimethoxy-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	yellow
45	2,5-dichloroaniline-4-sulphonic acid	„	yellow
46	3,4-dichloroaniline-5-sulphonic acid	„	yellow
47	1-aminobenzene-2-carboxylic acid	„	yellow
48	4-methylaniline-6-sulphonic acid	„	yellow
49	2-naphthylamine-1,7-disulphonic acid	„	reddish-yellow
50	2-naphthylamine-6,8-disulphonic acid	„	reddish-yellow
51	1-aminobenzene-2-sulphonic acid	„	yellow
52	4-amino-azobenzene-3,4'-disulphonic acid	„	red
53	4-amino-4'-acetamino-diphenyl-3-sulphonic acid	1-(2',5'-dimethoxy-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	orange

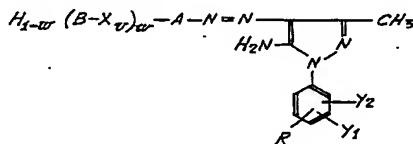
Example	diazo component	coupling component	shade
54	4-amino-diphenyl ether 3-sulphonic acid	1-(2',5'-dimethoxy- 4'- β -sulphatoethyl- sulphonyl)-phenyl-3- methyl-pyrazole- amine-(5)	reddish- yellow
55	4-amino-diphenylamine- 3-sulphonic acid	..	orange
56	3-amino-4-methyl- diphenyl-methane-2'- carboxylic acid	..	yellow
57	2-amino-4'-methyl- diphenyl sulphone-4- sulphonic acid	..	yellow
58	4-amino-1-(3'-nitro- benzoylamino)-benzene- 3-sulphonic acid	..	yellow
59	1-amino-benzene-4- sulphonic acid-2'- carboxy-phenylamide	..	yellow
60	4-amino-4'-acetamino- diphenyl-urea-3,3'- dicarboxylic acid	..	yellow
61	4-amino-4'-acetamino-di- phenyl-sulphide-2,2'- disulphonic acid	..	orange
62	3-amino-benzophenone- 4-ethyl-sulphone-2'- carboxylic acid	1-(2',5'-dimethoxy- 4'- β -sulphatoethyl- sulphonyl)-phenyl-3- methyl-pyrazole-amine- (5)	yellow
63	4-chloroaniline-2- sulphonic acid	1-(2'-methoxy-4'- β - sulphatoethylsulphonyl)- phenyl-3-methyl- pyrazole-amine-(5)	greenish- yellow
64	2,5-dichloroaniline-4- sulphonic acid	..	greenish- yellow
65	3,4-dichloroaniline-5- sulphonic acid	..	greenish- yellow
66	1-aminobenzene-2- carboxylic acid	..	greenish- yellow
67	4-methylaniline-2- sulphonic acid	..	greenish- yellow
68	2-naphthylamine-1,5- disulphonic acid	..	yellow
69	2-naphthylamine-1,7- disulphonic acid	..	yellow

Example	diazo component	coupling component	shade
70	2-naphthylamine-6,8-disulphonic acid	1-(2'-methoxy-4'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	yellow
71	2-naphthylamine-5,7-disulphonic acid	,,	yellow
72	4-amino-azobenzene-3,4'-disulphonic acid	,,	red
73	1-aminobenzene-2-sulphonic acid	,,	greenish-yellow
74	1-aminobenzene-4-sulphonic acid	,,	greenish-yellow
75	4-chloraniline-2-sulphonic acid	1-(2'-carboxy-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	greenish-yellow
76	1-aminobenzene-2-carboxylic acid	,,	greenish-yellow
77	2-naphthylamino-1,5-disulphonic acid	,,	yellow
78	4-amino-azobenzene-3,4'-disulphonic acid	,,	yellow
79	3,4-dichloro-aniline-5-sulphonic acid	,,	greenish-yellow
80	4-chloro-5-carboxy-aniline-2-sulphonic acid	,,	greenish-yellow
81	2-naphthylamine-6,8-disulphonic acid	,,	yellow
82	4-chloroaniline-2-sulphonic acid	1-(2'-sulpho-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	greenish-yellow
83	4-methylaniline-2-sulphonic acid	,,	greenish-yellow
84	2-naphthylamine-1,5-disulphonic acid	,,	yellow
85	2-naphthylamine-6,8-disulphonic acid	,,	yellow
86	1-aminobenzene-4-sulphonic acid	,,	greenish-yellow
87	4-aminoazobenzene-3,4'-sulphonic acid	,,	yellowish red

Example	diazo component	coupling component	shade
88	3,4-dichloroaniline-5-sulphonic acid	1-(2'-sulpho-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	greenish-yellow
89	4-chloro-5-carboxy-aniline-2-sulphonic acid	”	greenish-yellow
90	4-amino-benzene-sulphamide-3-sulphonic acid	”	yellow
91	4-amino-4'-nitro-diphenyl-amine-2-sulphonic acid	1-(2'-sulpho-5'- β -sulphoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	orange
92	4-chloroaniline-2-sulphonic acid	1-(2'-chloro-5'- β -sulphatoethylsulphonyl)-phenyl-3-methyl-pyrazole-amine-(5)	greenish-yellow
93	2,5-dichloro-aniline-4-sulphonic acid	”	greenish-yellow
94	3,4-dichloro-aniline-5-sulphonic acid	”	greenish-yellow
95	2-amino-4-chlorobenzene-carboxylic acid	”	greenish-yellow
96	2-naphthylamine-1,5-disulphonic acid	”	yellow
97	4-amino-azobenzene-3,4'-disulphonic acid	”	yellowish-red
98	4-chloro-aniline-2-sulphonic acid	1-(2'-methoxy-5'- β -acetoxy-ethylsulphonyl-phenyl)-3-methyl-pyrazole-amine-(5)	greenish-yellow
99	2-naphthylamine-1,5-disulphonic acid	1-(2'-methoxy-5'- β -methylsulphonloxy-ethylsulphonyl-phenyl)-3-methyl-pyrazole-amine-(5)	greenish-yellow
100	2-naphthylamine-1,5-disulphonic acid	1-[(2'-methoxy-5'- β -(N-methylsulphonyl-N-methyl-amino)-ethylsulphonyl-phenyl)]-3-methyl-pyrazole-amine-(5)	greenish-yellow
101	2-naphthylamine-1,5-disulphonic acid	1-(2'-methoxy-5'- β -phenylsulphonyloxy-ethylsulphonyl-phenyl)-3-methyl-pyrazole-amine-(5)	greenish-yellow

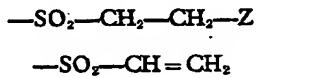
WHAT WE CLAIM IS:—

1. A dyestuff of the general formula



in which each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen or halogen atom or an alkyl, nitro, alkoxy, sulpho, carboxy, or carbonyl acylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents an aryl or aromatic-heterocyclic radical; X represents $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{N}=\text{N}-$, $-\text{CH}_2-$, $-\text{NH}-$, $-\text{NH}-\text{CO}-\text{NH}-$, $-\text{NH}-\text{CO}-$ or $-\text{NH}-\text{SO}_2-$; R represents a group of the formula

10 5 10 5



15 in which Z represents a hydroxy group or a radical capable of being split off by an alkaline agent; and each of v and w , which may be identical or different, represents zero or one.

15 15 20 20 25 25 30 30 35 35 40 40 45 45 50 50 55 55

2. A dyestuff as claimed in claim 1, wherein each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen or halogen atom or a, an alkyl having up to 4 carbon atoms, nitro, alkoxy having up to 4 carbon atoms, sulpho, carboxy, or carbonyl acylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents an aryl or aromatic heterocyclic radical that is either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from halogen atoms, sulpho, sulphamoyl, N-alkyl-sulphamoyl, N,N-dialkyl-sulphamoyl, N-aralkyl-sulphamoyl, N,N-diaryl-sulphamoyl, carboxy, carbamoyl, N-alkyl-carbamoyl, N,N-dialkyl-carbamoyl, N-aralkyl-carbamoyl, alkoxy carbonyl, aryloxycarbonyl, alkylsulphonyl, amino, N-alkylamino, N-aralkylamino, N-carbonyl acylamino, nitro, cyano, hydroxy, alkoxy, trifluoromethyl and alkyl groups, any alkyl groups having up to 4 carbon atoms; and X, R, v and w are defined as in claim 1.

3. A dyestuff as claimed in claim 1, wherein each of A and B which may be identical or different, represents a mononuclear or binuclear aryl or aromatic heterocyclic radical, that is either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from halogen atoms or sulpho, sulphamoyl, N-alkyl-sulphamoyl, N,N-dialkyl-sulphamoyl, N-alkyl-N-phenyl-sulphamoyl, N-phenyl-sulphamoyl, N-aralkyl sulphamoyl, N,N-diaryl sulphamoyl, alkyl-thio, benzylamino, carboxy, carbamoyl, N-alkyl-carbamoyl, N,N-dialkyl-carbamoyl, N-aralkyl-carbamoyl, N-phenyl-carbamoyl, alkoxy carbonyl, aryloxycarbonyl, arylsulphonyl, alkylsulphonyl, amino, N-alkylamino, N-phenyl-N-alkyl-amino, N,N-dialkylamino, alkanoylamino, arylcaronylamino, N-aralkylamino, nitro, cyclohexyl, cyano, hydroxy, alkoxy, phenoxyl, trifluoromethyl and alkyl groups, any phenyl radical being unsubstituted or substituted by one or more chlorine atoms or, alkyl, sulpho and/or carboxy groups; and Y_1 , Y_2 , X, R, v and w are defined as in claim 1.

4. A dyestuff as claimed in claim 1 or claim 3, wherein, in the grouping of the formula $-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{Z}$ represented by R, Z represents a halogen atom or an alkylsulphonyloxy, arylsulphonyloxy, alkylsulphonylamino, arylsulphonylamino, aliphatic carbonylacyloxy, aromatic carbonylacyloxy, phenoxy, dialkylamino, thiosulphato, phosphato or sulphato group.

5. A dyestuff as claimed in claim 2, wherein the grouping of the formula $-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{Z}$ represented by R, Z represents a halogen atom or a lower-alkylsulphonyloxy, arylsulphonyloxy, lower-alkylsulphonylamino, arylsulphonylamino, aliphatic or aromatic carbonylacyloxy, phenoxy, di-lower-alkylamino, thiosulphato, phosphato or sulphato group.

6. A dyestuff as claimed in claim 1, wherein each of Y_1 and Y_2 , which may be identical or different, represents a hydrogen, chlorine or bromine atom, a lower alkyl, lower alkoxy, nitro, sulpho, carboxy, lower alkanoylamino, benzamido, nitrobenzamido,

55 55

phenylsulphonylamino or *p*-tolylsulphonylamino group, with the proviso that only one of Y_1 and Y_2 may represent a hydrogen atom; each of A and B, which may be identical or different, represents a benzene, naphthalene or benzothiazole radical either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from chloro, bromo, sulpho, sulphamoyl, N-lower alkyl-sulphamoyl, N,N-di-lower alkyl-sulphamoyl, N-benzyl-sulphamoyl, carboxy, carbamoyl, N-lower alkyl-carbamoyl, N,N-di-lower alkylcarbamoyl, N-benzyl-carbamoyl, N-phenyl-carbamoyl, lower alkoxy-crabonyl, lower alkyl-sulphonyl, amino, lower alkylamino, acetamido, benzamido, nitrobenzamido, nitro, cyano, hydroxy, lower alkoxy, lower alkyl and trifluoromethyl groups; X represents $—O—$, $—S—$, $—CO—$, $—SO_2—$, $—N=N—$, $—CH_2—$, $—NH—$, $—NH—CO—NH—$, $—NH—CO—$ or $—NH—SO_2—$; R represents a group of the formula



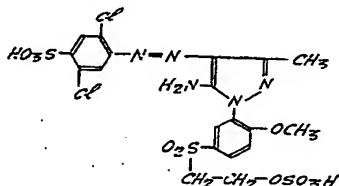
or

15 $—SO_2—CH=CH_2$ 15

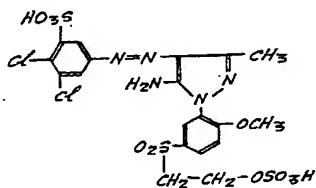
wherein Z represents a hydroxy, lower alkylsulphonyloxy, *p*-tolylsulphonyloxy, acetoxy, sulphobenzoxyloxy, phenoxy, di-lower alkylamino, thiosulphato, phosphato, sulphato, N-lower alkyl-sulphonyl-N-methyl-amino or phenylsulphonyloxy group; and each of v and w , which may be identical or different represents zero or one.

20 7. A dyestuff as claimed in claim 1, wherein each of A and B, which may be identical or different, represents a benzene, naphthalene or benzothiazole radical either unsubstituted or substituted by one or more substituents, which may be identical or different, selected from chloro, sulpho, carboxy, lower alkyl, lower alkoxy, lower alkanoylamino, benzamido, nitrobenzamido, nitro, cyano and N-phenyl-carbamoyl groups; and Y_1 , Y_2 , R, X, v and w are defined as in claim 6. 25

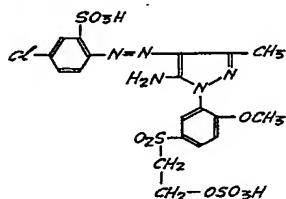
25 8. The dyestuff of the formula



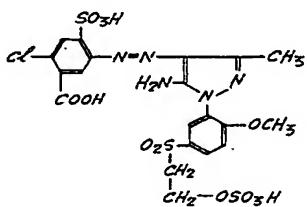
9. The dyestuff of the formula



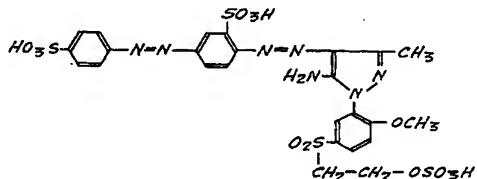
30 10. The dyestuff of the formula 30



11. The dyestuff of the formula



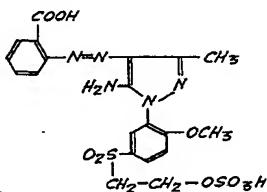
12. The dyestuff of the formula



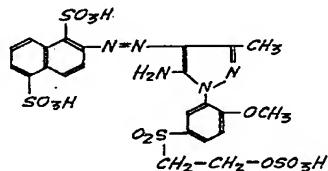
5

13. The dyestuff of the formula

5



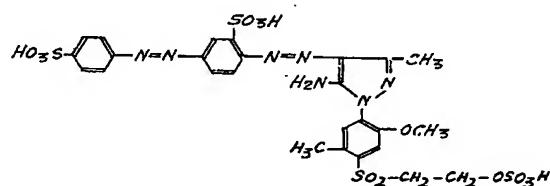
14. The dyestuff of the formula



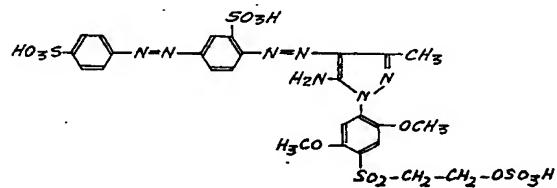
15. The dyestuff of the formula

10

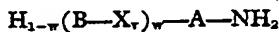
10



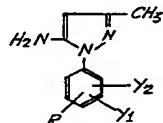
16. A dyestuff of the formula



17. A salt of a dyestuff as claimed in any one of claims 1, 3, 4, 6 and 7.
 18. An alkali metal salt of a dyestuff as claimed in any one of claims 1, 3, 4, 6 and 7.
 19. A salt of a dyestuff as claimed in claim 2 or claim 5.
 20. An alkali metal salt of a dyestuff as claimed in claim 2 or claim 5.
 21. A salt of a dyestuff as claimed in any one of claims 8 to 14.
 22. An alkali metal salt of a dyestuff as claimed in any one of claims 8 to 14.
 23. A salt of a dyestuff as claimed in claim 15 or claim 16.
 24. An alkali metal salt of a dyestuff as claimed in claim 15 or claim 16.
 25. A dyestuff as claimed in claim 1 and described in any one of the Examples herein.
 26. A process for the preparation of a dyestuff as claimed in claim 1, which comprises diazotizing a compound of the general formula



15 and reacting the resulting diazo compound with a compound of the general formula 15



in which formulae the symbols are defined as in claim 1, in a weakly acid or neutral medium or in a medium rendered alkaline by sodium bicarbonate or sodium carbonate.

27. A process as claimed in claim 26 carried out substantially as described in any one of the Examples herein. 20

28. A dyestuff as claimed in claim 1 whenever prepared by a process as claimed in claim 26 or claim 27. 20

29. A dyeing or printing process wherein a dyestuff as claimed in any one of claims 1 to 25 and 28 is used. 25

30. A process as claimed in claim 29, wherein a nitrogen-containing fibrous material or a cellulosic fibrous material is printed. 25

31. Material dyed or printed by a process as claimed in claim 30.

ABEL & IMRAY,
 Chartered Patent Agents,
 Northumberland House,
 303-306 High Holborn,
 London WC1V 7LH.